

Chlorinated Alcohols: IV. The Chlorination of Oleic Acid

J. E. MENTING, R. A. GRIMM, J. K. WEIL¹ and A. J. STIRTON,¹

Ashland Chemical Co., Bloomington, Minnesota 55420

3027

Abstract

Chlorination of oleic acid gave mainly 9,10-dichlorostearic acid but other products were also formed. By-products included the dimer, 9(10)-(9,10-dichlorostearoyloxy)-10(9)-chlorostearic acid, and the related trimer, formed independent of temperature in the range examined (-20 to $+29$ C). Higher solvent-oleic acid ratios decreased the amounts of dimer and trimer; chlorination in the presence of hydrogen chloride did not. The equivalent weight of 9,10-dichlorostearic acid was found to increase markedly upon treatment with chlorine and light, but in the dark the acid was apparently unchanged. These effects were independent of temperature.

Introduction

The reaction of elemental chlorine with oleic acid has received continuing attention over the years and this reaction is a route to 9,10-dichlorostearic acid (6,11). The kinetics of the reaction have been studied (10) and the formation of dimeric materials upon chlorination has been reported (4,5). Substitution reactions that can occur have been reported (12) to be proportional to temperature. However, not all these reports agree. In one case, no hydrogen chloride was evolved while in another case very significant amounts of substitution and hydrogen chloride were reported. Some report the addition is clean while others report a variety of products.

The goal of the work reported below was to optimize the addition of chlorine to oleic acid. Our approach involved identifying as many reaction products as possible and studying the effects of temperature, light and oleic acid concentration on product distribution.

Experimental Procedures

The oleic acid used in this work (97% 18 C mono-unsaturated <1% *trans*) was supplied by the Arizona Chemical Company. Vacuum distillation before use resulted in lighter colored chlorination products and more color-stable products. Tetrachlorostearic acid, used as a TLC reference compound, was prepared according to published (6) methods.

Chlorination Procedures

Typical Procedure. In most of the chlorinations a 500 ml three-necked flask was fitted with a gas dispersion tube, a stirrer and a thermometer. To this was added the solvent (175 ml) and oleic acid (50 g). The mixture was stirred, cooled and covered with towels or aluminum foil to prevent entry of light. Addition of chlorine resulted in an exothermic reaction, with a rise in temperature of 3 to 6 C. When the temperature fell the reaction was complete, and the mixture was concentrated on a rotary evaporator. During this concentration step the reaction mixture, saturated with chlorine, was exposed to light.

Dark Procedure. The chlorination was carried out as above except that the reaction flask and all the glass equipment between the chlorine cylinder and the reaction flask were covered with several layers of aluminum foil. Before the chlorine flow was started, all lights in the laboratory were shut off and the

windows were covered. When the chlorination was over the reaction mixture was concentrated in place and finally concentrated at 0.025 mm after all of the chlorine and most of the solvent were removed.

Procedure With Hydrogen Chloride. This was the same as the Dark Procedure except that hydrogen chloride was bubbled through the reaction mixture for 15 min before and also during the chlorination.

Isolation and Identification. The chlorination mixtures were analyzed by TLC in benzene-ether-acetic acid (85:14:1). Three components were observed and were numbered 1, 2 and 3. The R_f values were 0.41, 0.51, 0.55, respectively. See Figure 2.

These components were separated and purified by a combination of column chromatography (Skellysolve B-acetone-acetic acid, 50:49:1) and preparative TLC (benzene-ether-acetic acid, 85:14:1). A sample was first split into fractions by column chromatography. Analysis of the fractions showed which ones were enriched in the desired components and these fractions were then combined and finally purified by preparative TLC.

The identification of components 1, 2 and 3 was made as follows:

TLC Spot 1: This was the major component and the TLC behavior was indistinguishable from that of 9,10-dichlorostearic acid. The reference acid, mp 37.5–38.3 C, was prepared by recrystallization of a sample of chlorinated oleic acid from Skellysolve B. The infrared spectrum has bands at 3400–2400 cm^{-1} (broad, COOH), 3000–2800 cm^{-1} (s, CH), 1710 cm^{-1} (s, C=O), 1450 and 1375 cm^{-1} (m, CH), 1275 cm^{-1}

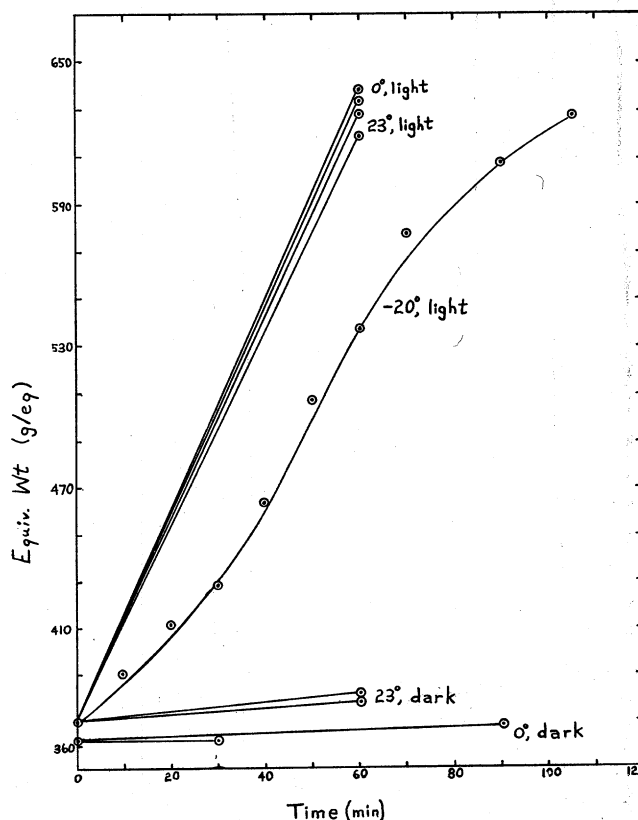


Fig. 1. Apparent equivalent weight of 9,10-dichlorostearic acid vs. time of chlorine treatment.

¹ E. Utiliz. Res. Dev. Div., ARS, USDA, Philadelphia, Pa.

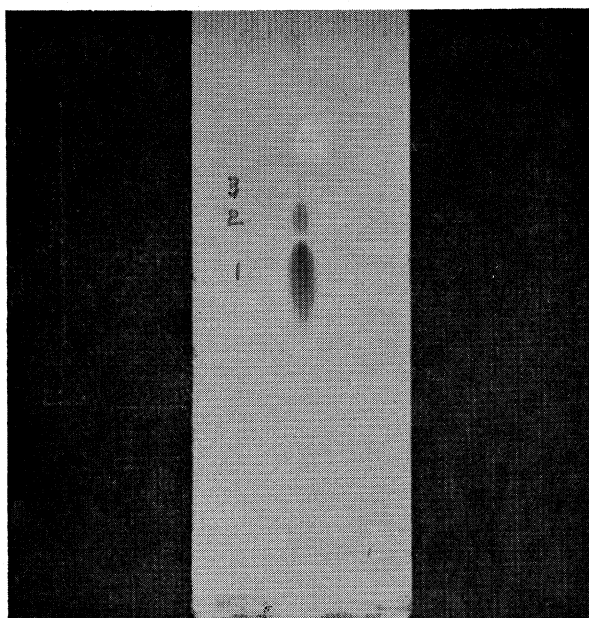


Fig. 2. TLC plate of a typical sample of chlorinated oleic acid showing spots 1, 2 and 3.

(m, C-O), 930 cm^{-1} (OH), 725 cm^{-1} (m, $-(\text{CH}_2)_n-$) and 640 cm^{-1} (C-Cl). The NMR spectrum has absorptions at $\delta 0.8$ – 2.5 ppm—several absorptions, relative intensity 31.1, theory 31 (0.8 – 1.1 ppm, relative intensity 3; 1.1 – 2.15 ppm, relative intensity 26; 2.15 – 2.5 ppm, triplet, relative intensity 2)— 3.8 – 4.2 ppm (multiplet, relative intensity 2, CHClCHCl-) and 11.3 ppm (singlet, relative intensity 1, COOH).

Since neither stearic acid nor 9,10,12,13-tetrachlorostearic acid were distinguishable from 9,10-dichlorostearic acid in any of the solvent systems, TLC Spot 1 may contain trace amounts of these compounds as impurities. Other polychloro-stearic acids from substitution reactions would probably be in this spot too. However, because of the elemental analyses and equivalent weight of the reaction mixtures, these must be present in only very small amounts.

TLC Spot 2: Recrystallization of chlorinated oleic acid resulted in the accumulation of compounds 2 and 3 in the mother liquor. Column chromatography and preparative TLC of the appropriate fractions gave several milligrams of pure TLC Spot 2, with carbonyl absorptions of equal intensity at 1710 and 1735 cm^{-1} (COOH and COOR) and a broad absorption at 1240 cm^{-1} (COOH) and 1170 cm^{-1} (COOR). The NMR spectrum (CDCl_3) showed absorptions at $\delta 0.9$ – 2.5 ppm—three groups of peaks, relative intensity 62, ($\delta 0.9$ – 1.05 , relative intensity 6; 1.05 – 2.1 , relative intensity 52; 2.1 – 2.5 , relative intensity 4)— 3.8 – 4.2 ppm (multiplet, relative intensity 3) and 4.9 – 5.2 ppm (broad, relative intensity 1). The NMR spectrum failed to show an absorption for the carboxyl proton. Compound 2 was shown to be an acid by IR and TLC. Thin-layer chromatography showed a streak in benzene-ether (75:25) and a spot in benzene-ether-acetic acid (75:24:1), the behavior to be expected for an acid (7). Failure to observe the carboxyl proton may be due to exchange with impurities in the NMR solvents (DCCl_3 and D_3CCOCD_3). Very small samples were used and the carboxyl proton would be present in low (1.4%) concentration.

The structure that best fits the data is that of 9(10)-chloro-10(9)-(9,10-dichlorostearoyloxy)stearic acid.

Analysis: Calculated for $\text{C}_{36}\text{H}_{67}\text{Cl}_3\text{O}_4$: %Cl, 15.87. Found: 16.19.

TLC Spot 3: About a milligram of a concentrate of this material was isolated. TLC of this concentrate showed it contained some of TLC spot 2, TLC spot 3 and a previously unseen spot moving just slightly faster than 3. The infrared spectrum of this concentrate showed a weak absorption from 3500 – 2400 cm^{-1} (COOH). The carbonyl absorptions were unequal, the band at 1735 cm^{-1} being about 1.5 times as intense as the band at 1710 cm^{-1} (COOR, COOH).

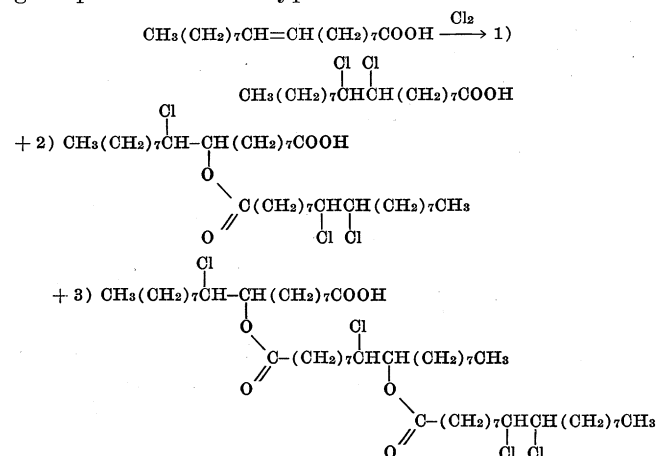
The Effect of Chlorine on 9,10-Dichlorostearic Acid

In a typical experiment, recrystallized 9,10-dichlorostearic acid (2 g) was dissolved in methylene chloride (8 ml) in a 15 ml round-bottomed flask and the solution was saturated with chlorine under different conditions of temperature and light, with the results shown in Figure 1. Except at -20°C duplicate experiments were run to minimize random error.

The clear glassy products showed only one spot in TLC. Increase in equivalent weight can be partly explained by increase in chlorine content; thus, equivalent weights of 634 and 691 were found to correspond to chlorine analyses of 50.55% and 36.89%, respectively.

Discussion

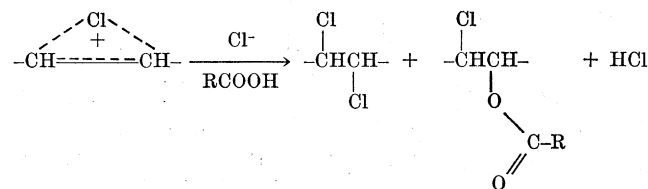
Our results show that chlorination of oleic acid in a solvent in the temperature range -20°C to $+28^\circ\text{C}$ gave products of the type:



At the usual concentration of 50 g of oleic acid per 175 ml of methylene chloride, the amounts of monomer, dimer and trimer were 86%, 13% and 1%.

At a given concentration the relative amounts of monomer, dimer and trimer were independent of temperature (experiments 1–4), and also of the nature of the solvent (CH_2Cl_2 , CHCl_3 , CCl_4 or Skellysolve F).

The reaction products can be rationalized by assuming a transition state that goes through a chloronium ion in the presence of chloride anions and carboxyl groups.



Since the main reaction product is 9,10-dichlorostearic acid, attack by the chloride anion predominates. Presumably this is a *trans* addition (9).

Participation of the carboxyl group could yield the dimeric ester-acid by intermolecular reaction or the monomeric cyclic ester by intramolecular reaction. The amount of participation depends on the concentration of carboxyl groups near the chloronium ion. Dilution of the reaction mixture with an inert solvent (experiment 5) suppressed intermolecular participation and there is no analytical evidence for intramolecular participation.

Evidence for Compound 3 is not as complete as that for Compound 2, but the structural assignment is believed to be correct. Considerations similar to those for dimer formation predict that not only must trimers be formed but higher telomers (2) also. The amounts of the higher telomers formed may be expected to decrease rapidly since, at the concentrations used, the ratio of participation to addition is a small fraction (about 1/7). In earlier work (12) the liberation of hydrogen chloride during the chlorination of oleic acid in the dark was regarded as evidence for substitution reactions. In the experiment reported, the production of hydrogen chloride began almost immediately, remained at a relatively constant rate during the chlorination, and then dropped when the double bonds were used up. These results can also be interpreted by telomer formation. As seen in the equation above, each molecule of ester that is formed results in one molecule of hydrogen chloride. Since in a chlorination mixture the concentration of carboxyl groups remains approximately constant during the chlorination, (ca. 14% decrease under our conditions) hydrogen chloride production would begin immediately and continue at a constant rate. When no more double bonds remained, no more ester formation would occur and hydrogen chloride production would drop. Roper (10) in his studies on the kinetics of chlorine addition to oleic acid used very dilute solutions and reported essentially no hydrogen chloride formation. These results are also consistent with the observation that in dilute solution very little dimer and therefore very little hydrogen chloride are formed.

Products resulting from a free radical reaction may also be formed during chlorination. These were not detectable by TLC in any of the solvent systems tried; in fact, none of the solvent systems were able to separate stearic acid, 9,10-dichlorostearic acid and 9,10,12,13-tetrachlorostearic acid. The free radical products were detected by measuring the equivalent weight of the sample (e.g. dichlorostearic acid) before and after chlorine treatment. Figure 1 shows that temperature had little effect but exposure to light was important. In the dark, at 0 or 23°C, equivalent weights were essentially unchanged but under similar conditions in light were nearly doubled. Part of the increase in equivalent weight is due to substitution as shown by the high chlorine content.

TABLE I
Chlorination of Oleic Acid
(50 g oleic acid/175 ml CH_2Cl_2)

Experiment	Temperature °C	Equivalent weight ^a	Cl ^b %	Dimer %	Trimer %
1	-20	375	19.5	11.0	1
2	-6	377	20.1	14.5	1
3	+5	380	20.0	12.5	1
4	+28	393	13.0	1
5 ^c	-18	359	20.4	2.0	..
6 ^d	+23	388	20.1	e	e
7 ^{d,e}	+23	380	e	e
8 ^{d,g}	0	404	e	e

^a Equivalent weight by titration (theory for dichlorostearic acid = 353). Iodine value was less than 0.5.

^b Theory per cent Cl for dichlorostearic acid = 20.07.

^c 50 mole excess of CHCl_3 .

^d Dark reactions.

^e By analytical TLC the amounts of dimer and trimer were essentially the same as in experiments 1-4.

^f Hydrogen chloride saturated solution (about 0.5 N HCl).

^g Solvent was 100 ml ethyl ether and 75 ml CH_2Cl_2 saturated with hydrogen chloride.

However, substitution of chlorine on the fatty chain cannot account for the total increase in equivalent weight and some other process may also occur.

If the concentration of chloride ion can be increased in the chlorination step, ester formation should be suppressed. This approach was effective in the chlorination of allyl alcohol (3) where it was found that in concentrated hydrochloric acid or in ether-hydrochloric acid solutions, the amount of dichloropropanol formed increased from 30-40% (inert solvents) to 50-70%. In our experiments, reaction mixtures were saturated with hydrogen chloride. This provided a mole ratio of hydrogen chloride to oleic acid of 2.5 in experiment 7 and 22 in experiment 8. Analytical TLC of the product from experiment 7 showed no significant reduction in telomer formation. The results from experiment 8 are less certain because ethers are known to participate in chlorinations (1) and the β -chloroethers that could form might behave like the β -chloroesters. TLC however showed no difference from other reaction mixtures.

ACKNOWLEDGMENTS

This work was done under contract with the USDA. The authors thank L. Clemens for many helpful discussions.

REFERENCES

- Dinulescu, I. G., M. Avram, C. T. Jijovici, M. Farcasin and C. D. Nenitzescu, *Chem. and Ind. (London)* 1964, 840-841.
- Grimm, R. A., J. E. Menting, A. J. Stirton and J. K. Weil, in press.
- Ing, H. R., *J. Chem. Soc.* 1948, 1393-1395.
- King, G., *Ibid.* 1949, 1817-1823.
- Leopold, B., and D. B. Mutton, *TAPPI* 42, 218-225 (1959).
- Lyness, W. I., and F. W. Quackenbush, *JAOCs* 32, 520-521 (1955).
- Mangold, H. K., *Ibid.* 33, 714 (1961).
- de la Mare, P. B. D., and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, 1966, p. 73-108.
- Poutsma, M. L., *Science* 157, 997-1005 (1967).
- Roper, G. H., *Chem. Eng. Sci.* 2, 18-26 (1953).
- Van Atta, G. R., D. F. Houston and W. C. Dietrich, *JAOCs* 24, 209-212 (1947).
- Veijola, V. E., *Suomen Kemistilehti* 31B, 307-308 (1958).

[Received September 10, 1968]